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Shafer, M.W.; Groot, R.A. de; Plechaty, M.M.; Scilla, G.J.

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CHEMICAL EVIDENCE FOR PEROXIDE IN $YBa_2CU_3O_7$

M. W. Shafer, R. A. de Groot*, M. M. Plechaty and G. J. Scilla IBM, T. J. Watson Research Center, Yorktown Heights, NY 10598

*EMS, Faculty of Sciences, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Dissolution studies on both normal ^{16}O and ^{18}O enriched $YBa_2Cu_3O_7$ in normal and ^{18}O enriched acid solutions were used to show that the origin of the evolved oxygen, which was determined by GC mass spectrometry, is from the solid and not the solvent. This implies strong oxygen-oxygen interactions indicative of peroxide formation, as predicted by de Groot et al(1), and is additional evidence that the oxygens are the hole carriers in these Cu-oxide superconductors.

1. INTRODUCTION

In order to formulate a mechanism(s) explaining high temperature superconductivity, experimental data in a number of areas are required. One of these is the nature of the hole-states in these Cu-oxide materials. It is generally recognized, for superconductivity to occur in this class of compounds, the presence of positive holes is necessary (2-4), and in fact they are a common denominator in both the $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ systems. Thus, La_2CuO_4 as a stoichiometric compound is non-superconducting but becomes so by doping with divalent alkaline earths or by stoichiometry variations. In $YBa_2Cu_3O_{6.5}$ no superconductivity occurs until hole-states are introduced by oxygen intercalation into the lattice. It was previously shown that the hole concentration can be determined directly by chemical means, and the superconducting transition temperatures scale directly with the hole concentration (5,6,7). Although it is not possible by this technique to determine the chemical identity of the particles carrying the holes, the only reasonable candidates are Cu^{3+} and the peroxide O_2^{2-}, which theory predicts may occur in these materials(1). One other conclusion one can draw from the chemical determination of holes is that whatever carries the holes is being transferred to the solution where it is reacted with ions such as Fe^{2+} or I^-. On the other hand, the dissolution of those compositions containing holes, i.e. those with $x > 6.5$, in the absence of oxidizable species (Fe^{2+} or I^-), results in the evolution of oxygen. This observation however does not allow one to distinguish between Cu^{3+} and peroxide, since both will lead to oxygen evolution. One possible way to distinguish between them is by determining the source of the evolved oxygen - whether it is from the solution or the solid.

It is well known that Cu-ions in aqueous solution are present as hydrated complexes, $[Cu(H_2O)_6]^{2+}$, and the hydrated water molecules are exchanged rapidly with other water molecules from the solvent(8). So it is likely that only a fraction of the oxygen atoms required for coordination of the Cu-ions in solution can originate from the sample. Although Cu^{3+} hydrated complexes are not stable in solution and will evolve oxygen, our earlier work showed that -if present- they live long enough to carry the hole into the solution. This means that they will certainly be hydrated before decomposition. Peroxides on the other hand do certainly not exchange oxygen atoms with the solvent because the $[O-O]^{2-}$ is much too strong. Thus, the oxygen evolved from a Cu^{2+} – peroxide species would most certainly originate from the peroxide group, hence directly from the sample. Therefore, a simple and direct experiment to determine the chemical nature of the hole-states is to do dissolution studies on ^{18}O enriched material. For example, if we dissolve a superconductor containing only ^{16}O in an ^{18}O enriched solution, if Cu^{3+} is the hole carrier we would expect the evolved oxygen to contain up to about 20% ^{16}O, depending on the lifetime of the Cu^{3+} complex compared with the rate of of water-exchange between the complex and the solution. If, on the other hand, the holes are carried by peroxides, we would expect 100% of the evolved oxygen to be ^{16}O. Similarly, we can dissolve an ^{18}O enriched solid in a pure ^{16}O solution. Here, if the hole carriers are peroxides, the evolved oxygen should be enriched in ^{18}O. The results of these experiments are described and it is concluded that the hole carriers in the Cu-oxide type superconductors are most certainly peroxides rather than Cu^{3+}

2. EXPERIMENTAL

The Y-Ba-Cu-oxides were prepared from the nitrates. The appropriate quantities of Cu metal (6N), assayed Y_2O_3 and $BaCO_3$ were dissolved in nitric acid, evaporated to dryness and converted to the oxide by heating in oxygen. After repeated heating and regrinding x-ray diffraction showed well crystallized single phase $YBa_2Cu_3O_x$. This oxygen content, x, of this material was then adjusted to 6.96 - 6.98, as determined by TGA and wet chemical analysis. It was then vacuum annealed at 550C and the resulting sample was a fine grained tetragonal powder with $x = 6.25$. It was used as the source material in the subsequent experiments.

Two series of sample were prepared from the source material, one containing normal oxygen, ^{16}O, and the other the isotope ^{18}O. The oxygen content of these samples was

controlled by heating the x = 6.25 material in pure oxygen at various temperatures until equilibrated and then rapidly quenching. The final x value was determined by TGA. HCl was used to dissolve the samples. The ^{18}O acid was prepared from 10% enriched H_2O.

The $^{18}O/^{16}O$ ratios in the gas evolved during acid dissolution were determined by gas chromatography / mass spectrometry (GC/MS). Isotopically enriched or standard $YBa_2Cu_3O_7$ (50-100 mg) were placed into a sealed reaction vial with 22 ml of enriched (10% ^{18}O) of H_2O. The enriched H_2O was purified by distillation just prior to use and purged with oxygen-free nitrogen for 10 min to remove dissolved oxygen. Acid was introduced by injecting 250- 500 uL of 50% HCl.

3. RESULTS AND DISCUSSION

Three experiments were done and the results are summarized in Table I. The first was the dissolution of $YBa_2Cu_3O_{6.98}$ (ybc) containing only ^{16}O in a solution containing only ^{16}O (Run #l); the second was the dissolution of the same ybc in an ^{18}O enriched solution (Run #2); the third was the dissolution of ^{18}O enriched ybc in acid containing only ^{16}O . In all cases the evolved oxygen was collected and the $^{18}O/^{16}O$ ratio determined as described above. We also determined the total ^{18}O concentration by SIMS. These results, on pressed powders, were always higher than the $\simeq$ 12% expected by the oxygenation of an x = 6.25 sample at 400 C. This shows that a temperature and pressure dependent exchange occurs between the ^{18}O gas phase and the lattice ^{16}O (9). The fact that GC/MS (which measures only the gases evolved) and SIMS (which measures the bulk composition) agree indicates that the data are representive of the materials bulk properties rather than some inhomogeneous surface process.

TABLE I

Run #	Solid	Solvent	$^{18}O/^{16}O$
1	ybc(16)	$H_2O(16)$	0.0030*
2	ybc(16)	$H_2O(18)$	0.0038
3	ybc(18)	$H_2O(16)$	0.43

* natural abundance $^{18}O/^{16}O$ = 0.002. The numbers in the parentheses, e.g.(18), indicate isotope enriched (^{18}O) or normal (^{16}O) ybc and solvent.

It is clearly seen from Run 2, that the evolved oxygen contains no ^{18}O. In fact, its composition is identical to that of Run 1, where the ybc was dissolved in a non-enriched HCl solution. In other words, the "holes" in the solid ybc, whether they are Cu^{3+} or O_2^{2-} are not reacting with the solvent (H_2O) to form gaseous O_2. If we now look at the results of Run 3, where the ^{18}O enriched ybc, containing the identical oxygen content, x = 6.98, is similarly dissolved in a non-enriched acid solution, we see the evolved oxygen is highly enriched in ^{18}O – by a factor of about 110, (compare Runs 2 and 3). Thus, we conclude unequivocally that when yttrium barium cuprate containing holes is dissolved in acid solution and oxygen is evolved, its origin is from the solid and not the solvent.

The question now becomes, what species in the solid would be more likely to form the O_2 molecule which is evolved in the dissolution process? The only two choices are, as discussed previously, $[Cu^{3+} - O^{2-}]^+$ and $[Cu^{2+} - O^-]^+$. Since O^{2-} ions have a $2p^6$ (neon) configuration with a valence of zero they have no tendency, either theoretically or experimentally, to form a covalent bond resulting in an O_2 molecule. In other words, an O^{2-} ion has nothing to gain from any covalent interactions (like any rare gas atom) but lots to lose - meaning O_2 formation from O^{2-} ions energetically impossible. The peroxy ion, O^-, on the contrary, has a $2p^5$ (fluorine) configuration with one unsaturated valence which can be used to form an oxygen- oxygen bond. Thus, the oxygen molecule evolved during the dissolution process originates from the interaction of two O^- ions. This conclusion that peroxide species are present in the lattice, is additional evidence that the oxygens are the hole carriers in these Cu-oxide superconductors. It should be pointed out that despite the fact that these are covalent materials and considerable mixing is thought to occur between Cu and oxygen, our data shows strong oxygen-oxygen interactions, indicative of peroxide formation.

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